International Journal of Environmental Sciences Vol. 4 No. 3. 2015. Pp. 144-149

Full Length Research Paper

Degradation of Pulp and Paper Mill Industrial Dyes by Indirect Electrochemical Method Using Carbon Electrodes

J. Narayana[a*], Spoorthi[a], and Prakash Kariyajjanavar[b]

[a]*Department of P.G. Studies & Research in Environmental Science, Kuvempu University, Jnana Sahyadri, Shankaraghatta, 577 451 Karnataka, India.*

[b]*Department of P.G. Studies & Research in Environmental Science, Gulbarga University, Kalaburagi, 585 106, Karnataka, India.*

**Corresponding author: J. Narayana*

Abstract

The indirect electrochemical method for pulp and paper mill industrial dyes was studied by using graphite carbon electrodes in laboratory scale. During the process, degradation of the chromoporic groups and aromatic rings of the dyes were proved by this method. The degradation of the dyes was followed using UV-Vis spectroscopy, LCMS, COD and TOC measurements. The maximum removal efficiency of colour 97% and 95%, chemical oxygen demand (COD) of 95% and 90% and total organic compound (TOC) of 95% and 97% could be achieved for the dyes at 2.5 g L^{-1} *of NaCl concentration, Current density of 340 A* m^{-2} *and at pH 3 for Basic green 1 and Direct Green 26, respectively. The effect of initial pH, supporting electrolyte and current density on the degradation of dye was discussed. The results revealed the suitability of the present process for the effective degradation of dyes pulp and paper mill dyes.*

Key words: carbon electrodes; industrial dye; LC-MS; TOC; UV-Vis

---

Introduction

The pulp and paper industry is the sixth largest polluter discharging a variety of gaseous, liquid and solid wastes into the environment (Ugurlu et al. 2006). Among the dyes family more than half are azo compounds used in industries like, paper, textile, rubber, plastic and cosmetics etc. After the dyeing process of azo dyes, due to their poor exhaustion properties as much as 30% of initial dye applied remain unfixed and end up in effluents (Prakash et al. 2012). The effluent generated during the processing of pulp and papers are highly colored. The dark color in untreated effluent is a major environmental concern as its discharge to water inhibits the photosynthetic activity of aquatic biota by reducing sunlight, besides exhibiting the toxic effects on biota (Deilek et al. 2001, Singh et al. 2002 and Merilainen et al. 2009). The presence of dyes in water is most undesirable, so a very small amount of these colouring agents are highly visible and may be toxic to the aquatic environment (Haddal et al. 2014).

The treatment of dye effluent is difficult and ineffective with conventional biological processes (Guven et al. 2009) and several physico-chemical methods because many synthetic dyes are very stable to light, temperature and are non-biodegradable nature of most dyes (Anouzla et al. 2009). In this context, electrochemistry is becoming a new alternative for wastewater treatment. The electrochemical method has proved to be effective in organic degradation, including aromatic compounds (Li et al. 2010). Indeed, electrochemical method has been successfully tested and it has certain significant advantages such as simple equipment, easy operation and lower operating cost (Dirany et al. 2012, Akbal et al. 2011, Chu et al. 2013, Hongzu et al., 2007). The process requires significantly less equipment than conventional biological treatment processes (Prakash et al. 2011(a), Li et al. 2008). In the past, graphite was frequently used as an anode for the electrochemical degradation of textile dye as it is relatively cheaper and gives satisfactory results (Prakash et al. 2013). The aim of this work was to test the feasibility of electrochemical method for the degradation of pulp and paper mill industrial dyes using graphite carbon electrodes.

Materials and Methods

Experimental Part

Materials

The commercial pulp and paper mill industrial dyes Basic green 1 (CAS no. 633-03-04) and Direct Green 26 (CAS no. 6388-26-7) were collected at Mysore Paper Mill Industry, Bhadravathi, India. All other chemicals used for the experiments were of analytical grade reagents and obtained from s d fine chem-limited, Mumbai, India. Cylindrical carbon electrodes (Chemical composition: graphite carbon + coke: 85% and ash 15%) were obtained from Power Cell Battery India Limited. A digital DC power supply (AESC: 30V, 2A) was used as an electrical source. Double distilled water was used to prepare the desired concentration of dye solutions and the reagents.

Instrumentation

Electrochemical degradation studies

Graphite carbon electrodes of 4.5 cm length and 0.8 cm diameter were used as anode and cathode for electrochemical degradation studies (Prakash et al. 2011(b)). The effective electrode area was 12.32cm^2. The supporting electrolytes such as NaCl and Na_2SO_4 were added to the electrolytic solution, which increases the conductivity of the solution and reduces the electrolysis time. The solution was kept under agitation using magnetic stirrer.

UV-Visible studies

A UV-Vis Spectrophotometer (UV-2602) was employed to measure the optical density of dye solution (λ_{max}: 437 nm for Basic green 1, λ_{max}: 629 nm for Direct Green 26) before and after electrolysis. The decolourisation efficiency was calculated using the relation:

$$\%E= ((A_i-A_f)/A_i) \times 100 \qquad (1)$$

Where; A_i and A_f are absorbance values of dyes solutions before and after treatment with respect to their λ_{max}, respectively or A_i and A_f are initial and final COD and TOC values of the dyes solutions, respectively.

Liquid Chromatography-Mass Spectrometry studies (LC-MS).

The extent of degradation of dye samples were analyzed by LC-MS studies (LCMS-2010A, Shimadzu, Japan). The LC-MS was fitted with column C18. The mobile phase was methanol: water (90:10). The flow rate was 0.2 mL min^{-1} and the injection volume of dye was 5µL. The dye solutions were injected into LC column before and after electrolysis. Analyses using ESI (electron spray ionization) interface were done under the same chromatographic conditions as described for the APCI (atmospheric pressure chemical ionization) analysis, except the guard column, which was not used in the ESI analysis.

Results and Discussion

This study were conducted by taking 200 mL of simulated dye concentration of 50 ppm (w/v) to study the effect of controlling parameter like, solution *p*H, Contact time, dosage of electrolyte and current density by maintaining in constant agitation at room temperature.

Influence of electrolysis conditions on dye degradation

Effect of initial pH

Solution *p*H is one of the important factors that affect the performance of electrochemical process. Hence, experiments were conducted to study the effect of *p*H on the degradation efficiency of Basic green 1 and Direct Green 26. The initial *p*H of the solution (3-11) was adjusted using 1M H_2SO_4 or NaOH (Yi et al. 2008). The electrolysis was carried out at the current density of 340 A m^{-2} for 30 min. From the UV-Vis spectra (Fig.1), it was clear that, the absorbance in the visible region is attributed to the presence of chromophores (Prakash et al. 2011(b)). In acidic *p*H, during electrochemical degradation, the cleavage aromatic rings have taken place, which results in the decrease of optical density of the dye solution, which indicated the degradation of larger dye molecules into smaller fragments (Fatiha et al. 2006). However, the active chlorine can lead the partial mineralisation of dyes (Yi et al. 2008). In acidic *p*H decolouration efficiency of Basic green 1 and Direct Green 26 was found to be 97% and 95%, respectively (Fig.1). The results indicated that after electrolysis the final *p*H was remained almost same in acidic and neutral conditions and decreased at basic condition. In acidic solution the degradation process of dyes were found higher than that of the basic solution, since in acidic solutions chlorides are reduced to free chlorine (Vlyssides et al. 1999), which is a dominant oxidizing agent (Chatzisymeon et al. 2006). Therefore the optimum *p*H 3 was maintained in subsequent experiments.

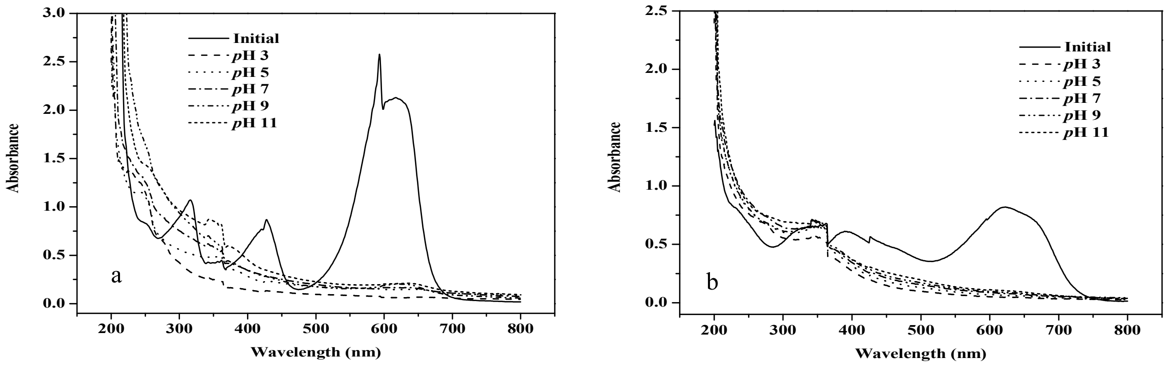

Fig. 1. Absorption spectra for (a) Basic green 1 and (b) Direct Green 26 dyes solution initial and after electrolysis at different *p*H. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); electrodes: graphite carbon; NaCl: 2.5 g L^{-1}; current density: 340 A m^{-2}; time: 30 min.

Effect of supporting electrolytes

In UV-Vis spectra, as can be seen from the Fig. 2, the addition of NaCl to the dyes solutions during electrolysis, the decolourisation efficiency increased for Basic green 1 and Direct Green 26. From this observation it was concluded that the introduction of NaCl as electrolyte can enhance the degradation efficiency and shortens electrolysis time, which may be attributed to the reaction between the electrogenerated chlorine/hypochlorite and the dye molecule (Prakash et al. 2011(b).

Moreover, the increased concentration of NaCl results in a decrease in the operating voltage at the given current density (Prakash et al. 2011(b). Increase in the concentration of NaCl up to 2.5 g L^{-1} accelerated the degradation rate, enabling the decolourisation efficiency of Basic green 1 (Fig. 3a) and Direct Green 26 (Fig. 3b) to 97 % and 95 %, respectively. A further increase in NaCl concentration (> 2.5 gL^{-1}) there was a slight improvement in decolourisation efficiency, and therefore the optimal concentration of NaCl in successive degradation studied was fixed at 2.5 g L^{-1}.

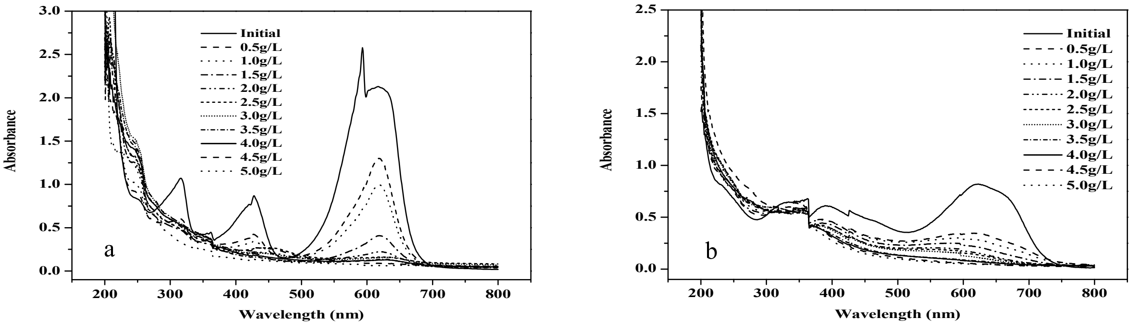

Fig. 2. Absorption spectra for (a) Basic green 1 and (b) Direct Green 26 dyes solutions before and after electrolysis (30 min) at increase of NaCl concentration. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); electrodes: graphite carbon; pH: 3; current density: 340 A m^{-2}; time: 30 min.

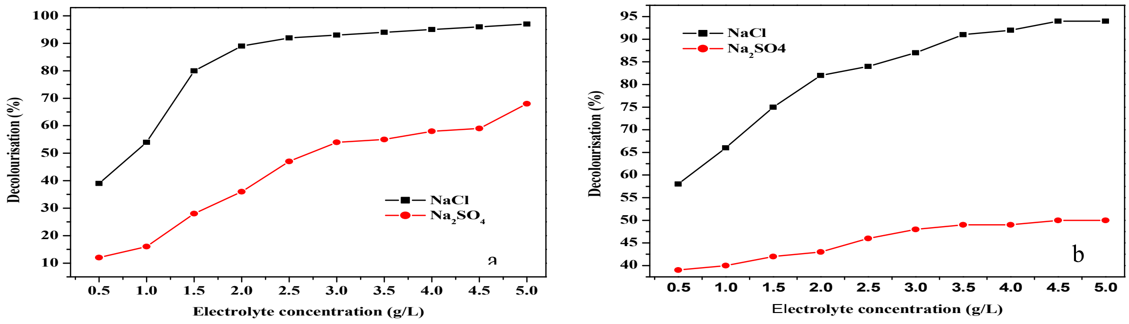

Fig. 3. Effect of supporting electrolytes (a) NaCl and (b) Na_2SO_4 on decolourisation efficiency of the dye (a) Basic green 1 and (b) Direct Green 26 dye solutions. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); electrodes: graphite carbon; pH: 3; current density: 340 A m^{-2}; time: 30 min

Whereas compare to the effect of Na_2SO_4, the decolourisation efficiency was found to be lower than that of NaCl. The higher decolourisation efficiency in presence of NaCl is attributed to the generation of more powerful oxidizing agents such as Cl_2, HOCl and OCl^-. The decolourisation in presence of Na_2SO_4 is attributed to the generation of persulfate ions that can oxidize organic dyes (Yi et al. 2008).

Effect of current density

The electrolysis of dye solution was carried out at different current densities (85, 170, 255, 340 and 425 A m^{-2}) at graphite carbon electrodes to investigate the influence of current density on the degradation efficiency of Basic green 1 and Direct Green 26 keeping NaCl concentration at 2.5 g L^{-1}, dye concentration at 50 ppm (w/v), *p*H at 3 and at room temperature. It can be found that decolourisation efficiency (Fig. 4) increased with increasing the applied current density (Abu Ghalwa et al 2005). This is because of the increased rate of generation of oxidants, such as chlorine/hypochlorite and hydroxyl radicals at higher current densities. Up to a current density of 340 A m^{-2}, the degradation efficiency of both the dyes was increased almost linearly. At higher current densities (>340 A m^{-2}) the degradation efficiency was attained almost constant. Also the energy consumption was found to be more at higher current densities with a subsequent stripping of electrodes (Rajkumar et al. 2007). Therefore, the optimal current density for the successive electrochemical degradation was fixed at 340 A m^{-2}.

Analysis of COD & TOC

In the present study it can be seen that the degradation of Basic green 1 and Direct Green 26 from their aqueous solutions may proceed by indirect electrochemical oxidation rather than direct electrochemical process. The maximum COD of 95% and 90%

and TOC of 95% and 97% could be achieved for the dyes at 2.5 g L^{-1} of NaCl concentration, current density 340 A m^{-2} at pH 3 for Basic green 1 and Direct Green 26, respectively. The electrolysis was carried out at a current density of 340 A m^{-2}. At this current density, Cl_2 generated in the solution drives the oxidation process. The Cl_2 species is a powerful oxidizing agent capable of oxidizing the dyestuffs. In the absence of chloride containing electrolytes, the COD, TOC removal and dye degradation efficiency was very low (Abu Ghalwa et al 2005). The percent removal of COD and TOC found to be increased with increase in the concentration of NaCl. This confirmed that the electrogenerated chlorine/hypochlorite will play an important role in the electrochemical degradation process of the dyestuffs.

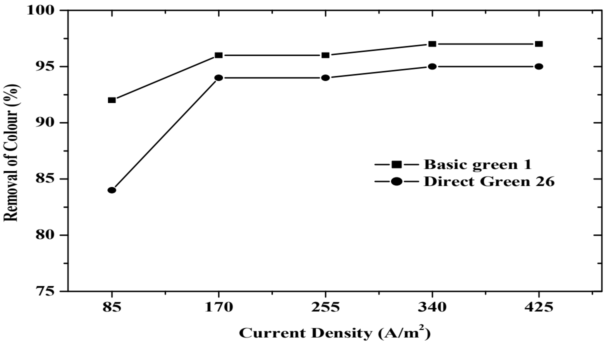

Fig. 4. Effect of current densities on decolourisation of dyes (a) Basic green 1 and (b) Direct Green 26. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); *p*H: 3; NaCl: 2.5 g L^{-1}; current density 340 A m^{-2}; time: 30 min.

Liquid Chromatography-Mass Spectrometry studies (LC-MS)

LC–MS studies were employed to monitor the diminution in mass of the fragments of Basic green 1 and Direct Green 26 dyes before and after electrolysis. MS spectrum of the dyes recorded before electrolysis shows more number of peaks at higher m/z values due to the presence of dyes and other impurities (Figure 5a and 6a).

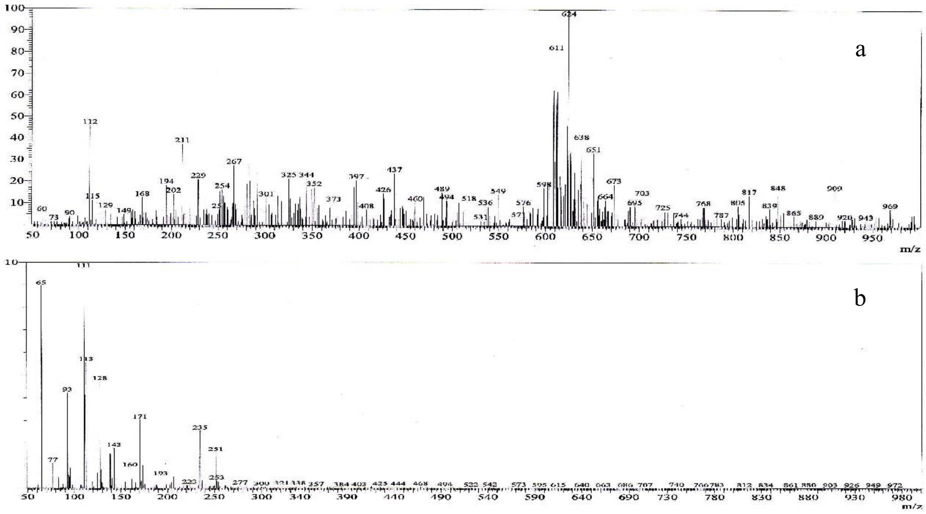

Fig. 5. Mass spectrum of Basic green 1: (a) before electrolysis, (b) after electrolysis. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); electrodes: graphite carbon; *p*H: 3; current density 340 A m^{-2}; time: 30 min.

The MS spectrum of the filtrate solution after complete electrolysis shows the absence of majority of the peaks (Figure 5b and 6b). This clearly indicated that almost all dye was coagulated and removed in the form of sludge. The remaining peaks at low m/z values in the mass spectra may be due to the presence of substituted simple aromatic compounds.

Electrical Energy Consumption

The major operating cost is associated with the electrical energy consumption during electrochemical degradation process. The electrical energy consumption (E) is required to decompose 50 ppm (w/v) Basic green 1 and Direct Green 26, dye solutions at various current densities was calculated using the relation:

$$E=((VIt_E) / V_s)\times 10^{-3}$$

Where; E is the electrical energy consumption (k W h m^{-3}), V is the applied voltage (V), I is the applied current (A), t_E is the electrolysis time (h) and V_s is the volume of dye solution (m^3). As per the results, the minimum electrical energy consumption was 10.70 k W h m^{-3} at 340 A m^{-2} current density. At higher current densities, the energy consumption was found to be increased and it may be attributed to the increased hydrogen and oxygen evolution reaction (Table 1).

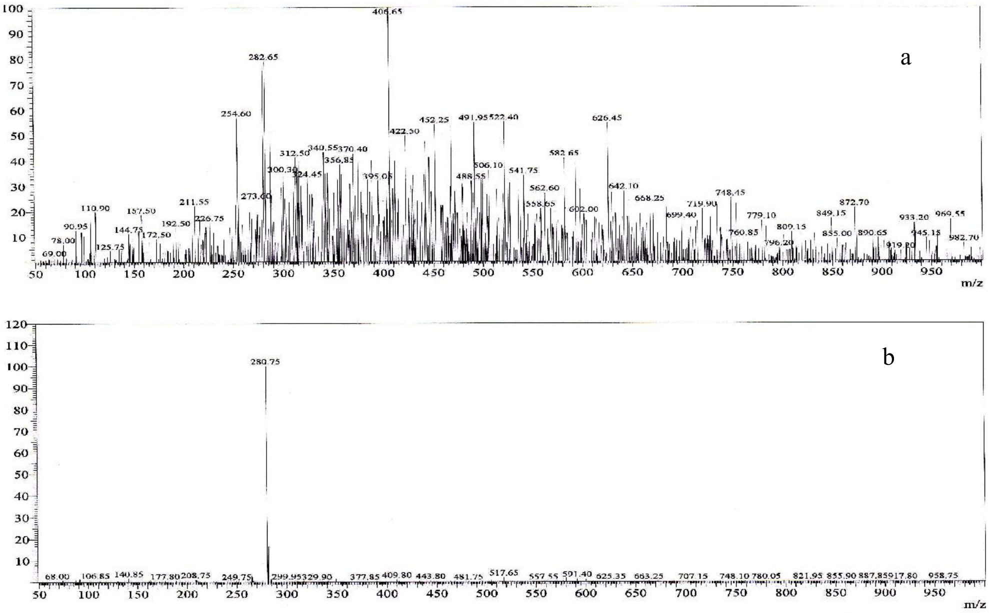

Fig. 6. Mass spectrum of Direct Green 26: (a) before electrolysis, (b) after electrolysis. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); electrodes: graphite carbon; *p*H: 3; current density 340 A m^{-2}; time: 30 min

Current density (Am^{-2})	Energy Consumption (k Wh m^{-3})	Degradation (%)	
		Basic green 1	**Direct Green 26**
085	1.308	92	84
170	3.267	96	94
255	6.575	96	94
340	10.700	97	95
425	16.667	97	95

Table 1: The electrical energy consumed during electrochemical degradation of Basic green 1 and Direct Green 26 dye solutions (50 ppm, w/v); Electrolysis time 30 min:

Conclusion

In the present work the electrochemical degradation of Basic green 1 and Direct Green 26 was carried out using graphite carbon as anode and cathode, in the optimal operating conditions (current density 340 A m^{-2}, NaCl concentration 2.5 g L^{-1} and at room temperature. Increasing the initial *p*H will lead to corresponding decrease in the degradation efficiency of dyes. The effect of conducting salt clearly showed that the introduction of Cl^{-} containing electrolytes enhance the degradation efficiency of the dye. UV-Vis and MS spectral studies confirmed that the proposed electrochemical degradation process is an effective method for the degradation of Basic green 1 and Direct Green 26.

Acknowledgements

The Authors are grateful to UGC, New Delhi for the financial support extended. Also grateful to Kuvempu University, Power Cell Battery India Limited, Mysore Paper Mill Industry, Bhadravathi, India for their support to carry out this work.

References

Abu Ghalwa, N.M. and Abdel-Latif, M.S. (2005). Electrochemical Degradation of Acid Green Dye in Aqueous Wastewater Dyestuff Solutions Using a Lead Oxide Coated Titanium Electrode, J. Iran. Chem. Soc. 2: 238-243.

Akbal, F. and Kuleyin, A. (2011). Decolorization of Levafix Brilliant Blue E-B by Electrocoagulation Method, Environmental Progress & Sustainable Energy, 30: 29-36.

Anouzla, A. Abrouki, Y. Souabi, S. Safi, M. and Rhbal. H. (2009). Colour and COD removal of disperse dye solution by a novel coagulant: Application of statistical design for the optimization and regression analysis, J. Hazard. Mater. 166: 1302–1306.

Chatzisymeon, E. Xekoukoulotakis, N.P. Coz, A. Kalogerakis, N. and Mantzavinos, D. (2006). Electrochemical treatment of textile dyes and dye stuff effluents, J. Hazard. Mater. 137:998-1007.

Chu, Y. Zhang, D. Liu, L. Qian, Y. and Li, L. (2013). Electrochemical degradation of m-cresol using porous carbon-nanotube-containing cathode and Ti/SnO2-Sb2O5–IrO2 anode: Kinetics, byproducts and biodegradability, J. Hazard. Mater. 252: 306-312.

Deilek, F.B. and Bese, S. (2001). Treatment of pulping effluents using alum and clay-color removal and sludge characteristics, Water SA, 27: 361-366.

Dirany, A. Sires, I. Oturan, N. Ozcan, A. and Oturan, M.A. (2012). Electrochemical treatment of the antibiotic sulfachloropyridazine: kinetics reaction pathways, and toxicity evolution, Environ. Sci. Technol. 46: 4074–4082.

Fatiha, A. Mouffok, R.G. Belhadj, M. Addou, A. and Brisset, J. (2006). Bleaching and Degradation of textile dyes by nonthermal plasma process at atmospheric pressure, Ind. Eng. Chem. Res. 45: 23-29.

Guven, G. Perendeci, A. and Tanyolac, A. (2009). Electrochemical treatment of simulated beet sugar factory wastewater, Chemical Engineering Journal 151: 149–159.

Haddal, M.E. Regti, A. Laamari, M.R. Mamouni, R. and Saffaj, N. (2014). Use of Fenton reagent as advanced oxidative process for removing textile dyes from aqueous solutions, J. Mater, Environ. Sci 5 (3): 667-674.

Hongzu, M. Bo, W. And Xiaoyan, L. (2007). Studies on degradation of Methyl Orange wastewater by combined electrochemical process, J. Hazard. Mater. 149: 492-498.

Li, F. Yanwei, Z. Weishen, Y. Guohua. C. and Fenglin. Y. (2008). Electrochemical degradation of aqueous solution of Amaranth azo dye on ACF under potentiostatic model, Dyes Pigm. 76: 440-446.

Li, M. Xueb, Q. Zhang, Z. Feng, C. Chen, N. Lei X. Shen, Z. and Sugiura. N. (2010). Removal of geosmin (trans-1,10-dimethyl-trans-9-decalol) from aqueous solution using an indirect electrochemical method, Electrochimica Acta 55: 6979–6982

Merilainen, P. and Oikari, A. (2009). Exposure assessment of fishes to modern pulp and paper mill effluents after black liquor spil, Environment Monitor Assessment, 144: 419-435.

Prakash, K. Narayana, J. and Arthoba, Y. N. (2011(a)): Degradation of Textile Wastewater by Electrochemical Method. Hydrol Current Res 2 110. doi:10.4172/2157-7587.1000110

Prakash, K. Narayana, J. and Arthoba, Y. N. (2011(b)). Studies on degradation of reactive textile dyes solution by electrochemical method, J. Hazard. Mater. 190: 952–961.

Prakash, K. Narayana, J. and Arthoba, Y. N. (2013) .Electrochemical Degradation of C.I. Vat Brown1 Dye on Carbon Electrode, Advanced Chemistry Letters, 1: 32–39.

Prakash, K. Narayana, J. Arthoba Y.A. and Kalachar. H. C. B (2012) Electrochemical Degradation and Cyclic Voltammetric Studies of Fast Sulphon Black F and Eriochrome Black T: A Comparative Study, Inventi Impact: Water & Environment 2012 (3): 139-144

Rajkumar, D. Song, B. J. and Kim, J.G. (2007). Electrochemical degradation of Reactive Blue 19 in chloride medium for the treatment of textile dyeing wastewater with identification of intermediate compounds, Dyes Pigments 72: 1-7.

Singh, A. Agarwal, S.B. Rai, J.P.N. and Singh, P. (2002). Assessment of the pulp and paper mill effluent on growth, yield and nutrient quality of heat (Triticum aestivum L), Journal of Environmental Biology 23:283-288.

Ugurlu, M. Karaoglu, M. H. and Kula, I. (2006). Experimental Investigation of Chemical Oxygen Demand, Lignin and Phenol Removal from Paper Mill Effluents Using Three-Phase Three-Dimensional Electrode Reactor, Polish J. of Environ. Stud. 15 (4): 647-654

Vlyssides, A.G. Loizidou, M. Karlis, P.K. Zorpas, A.A. and Papaioannou, D. (1999). Electrochemical oxidation of a textile dye wastewater using a Pt/Ti electrode, J. Hazard. Mater. B70: 41-52.

Yi, F. Chen, S. and Yuan, C. (2008). Effect of activated carbon fiber anode structure and electrolysis conditions on electrochemical degradation of dye wastewater, J. Hazard. Mater. 157: 79-87.